655-48-1; *meso*-**3b**, 5173-29-5; (±)-**3b**, 5173-28-4; *meso*-**3c**, 37580-81-7; (±)-**3c**, 69483-09-6; *meso*-**3d**, 37580-82-8; (±)-**3d**, 126082-50-6; *meso*-**3e**, 86001-18-5; (±)-**3e**, 86001-17-4; *meso*-**3f**, 126082-51-7; (±)-**3f**, 126082-52-8; zinc, 7440-66-6; zinc dichloride, 7646-85-7; benzophenone, 119-61-9; *p*-tolyl ketone, 611-97-2; *p*-chlorophenyl ketone, 90-98-2; *p*-chlorobenzophenone, 134-85-0; fluoren-9-one, 486-25-9; anthrone, 90-44-8; 9-xanthone, 90-47-1; 1,1,2,2-tetraphenylethylene glycol, 464-72-2; 1,1,2,2-tetra-*p*-tolylethylene glycol, 913-86-0; 1,1,2,2-tetrakis(*p*-chlorophenyl)-ethylene glycol, 5418-23-5; *meso*-1,2-bis(*p*-chlorophenyl)-1,2-diphenylethylene glycol, 126082-53-9; *dl*-1,2-bis(*p*-chlorophenyl)-1,2-diphenylethylene glycol, 126082-54-0; fluorenopinacol, 3073-51-6; anthrapinacol, 4393-30-0; xanthopinacol, 6272-59-9; acetophenone, 99-90-1; *p*-bromoacetophenone, 99-90-1; *p*-cyanoacetophenone, 1443-80-7; *meso*-2,3-diphenyl-2,3-butanediol, 4217-65-6; *dl*-2,3-diphenyl-2,3-butanediol, 22985-90-6; *meso*-2,3-bis(*p*-bromophenyl)-2,3-butanediol, 126082-55-1; *dl*-2,3-bis(*p*-bromophenyl)-2,3-butanediol, 126082-56-2; *meso*-2,3-bis(*p*-cyanophenyl)-2,3-butanediol, 93453-78-2; *dl*-2,3-bis(*p*-cyanophenyl)-2,3-butanediol, 93453-76-0.

Bromo[3]cumulene and Bromo Enyne Radical Cyclization to Cyclopentenyne Products†

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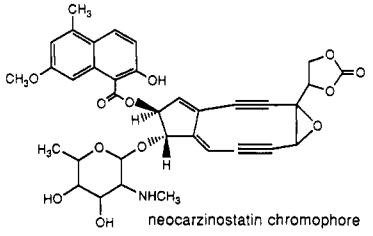
The synthetic utilization of halo[3]cumulenes is new and holds considerable potential for the development of novel methodology.[1] Recently, we reported a new halo enyne synthesis in which the key step was a regioselective S_N2' halide displacement on bromo[3]cumulenes.[2] In this work we present our studies directed toward the vinyl radical cyclization of appropriately substituted bromo[3]cumulene and bromo enyne intermediates. The synthetic targets chosen are substituted cyclopentenynes. This structural moiety is part of the highly strained fused ring system of neocarzinostatin, an extremely potent antitumor antibiotic, whose structure was recently elucidated.[3] The methodology described herein could find an application that compliments the present synthetic approaches to neocarzinostatin.[4]

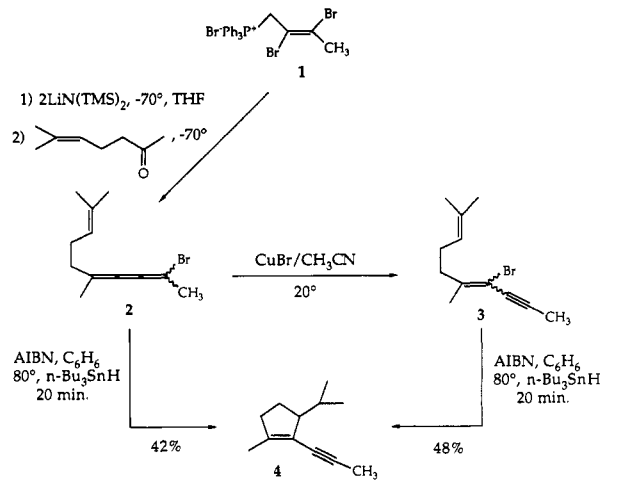


neocarzinostatin chromophore

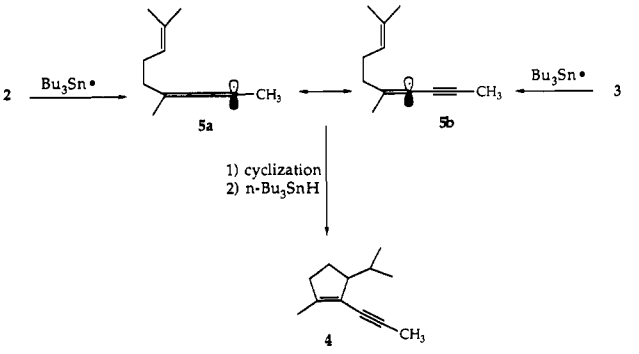
The synthetic method to be described is presented in Scheme I. The bromo[3]cumulene **2** was prepared from phosphonium salt **1** and 6-methyl-5-hepten-2-one by a Wittig condensation. Thus, **2** was converted to the bromo enyne **3** as reported.[2,5] When either **2** or **3** was treated with 1.1 equiv of *n*-Bu_3SnH (AIBN initiation) in refluxing benzene (0.02 M) for 20 min, the 5-(*π-Endo*)-*Exo-Trig* cyclization[6] product **4** was isolated. Yields of **4** in each case were based on the starting phosphonium salt **1**. Cyclopentene formation via **2** (42%, two steps) was similar to that via the intermediacy of **3** (48%, three steps).[7,8]

†Dedicated to the memory of Dr. Daniel F. Lieberman, a friend and colleague.

Scheme I



Scheme II



A logical mechanistic rational for this radical cyclization is presented in Scheme II. Bromo[3]cumulene **2** and bromo enyne **3** are converted to the same planar radical intermediate represented as forms **5a** and **5b** under these

(1) Ziegler, C. B., Jr.; Harris, S. M.; Baldwin, J. E. *J. Org. Chem.* **1987**, *52*, 443.

(2) Ziegler, C. B., Jr. *Tetrahedron Lett.* **1988**, *28*, 411.

(3) Structure: Edo, K.; Mizugaki, M.; Koidi, Y.; Seto, H.; Furihata, K.; Otaki, N. and Ishida, N. *Tetrahedron Lett.* **1985**, *26*, 331. Myers, A. G.; Proteau, P. J.; Handel, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 7212. Proposed mode of biological action: Myers, A. G. *Tetrahedron Lett.* **1987**, *28*, 4493. Myers, A. G.; Proteau, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 1146. Hensens, O. D.; Goldberg, I. H. *J. Antibiotics* **1989**, *42*, 761. Hensens, O. D.; Giner, J.-L.; Goldberg, I. H. *J. Am. Chem. Soc.* **1989**, *111*, 3295.

(4) Relevant synthetic work: Wender, P. A.; Harmata, M.; Jeffrey, D.; Mukai, C.; Suffert, J. *Tetrahedron Lett.* **1988**, *29*, 909. Myers, A. G.; Widdowson, L. *Ibid.* **1988**, *29*, 6389. Myers, A. G.; Fundy, P. A.; Lindstrom, P. A. Jr. *Ibid.* **1988**, *29*, 5609. Hirama, M.; Fujiwara, K.; Shigematu, K.; Fukazawa, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4120.

(5) As was demonstrated in ref 2, the bromo[3]cumulene products of unsymmetrical ketones are formed as a 1:1 geometrical pair. Thus, bromo enynes synthesized from them are isomeric.

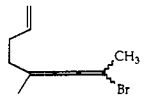
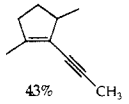
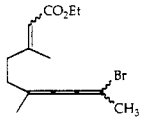
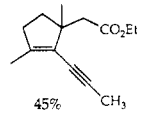
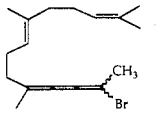
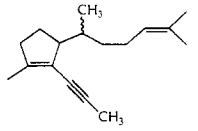
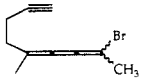
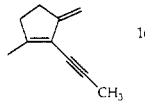
(6) The term (*π-Endo*) used here to describe this type of vinyl radical has been coined by Crich; see: Crich, D.; Fortt, S. M. *Tetrahedron Lett.* **1987**, *27*, 2895. Intramolecular vinyl radical cyclizations have been demonstrated by many. For some pertinent examples, see: Julia, M. *Acc. Chem. Res.* **1971**, *4*, 1971. Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321. Beckwith, A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525. Curran, D. P.; Rakiewicz, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 1448. Curran, D. P.; Kuo, S.-C. *Ibid.* **1986**, *108*, 1106. Stork, G.; Mook, R., Jr. *Ibid.* **1987**, *109*, 2829: Munt, S. P.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1989**, 480.

(7) It was not prudent to determine the isolated yield of **2** in this work. The bromo[3]cumulene **2** readily decomposed when concentrated. Ease and expediency were best served when **2** was kept unpurified in solution. The yield of **3**, however, from **1** was 57%. Cyclization of **3** to **4** occurred in 85% isolated yield, thus giving a combined total of 48% from **1**.

(8) The cyclopentene **4** was also prepared in 44% overall yield from **1** via syringe pump addition of *n*-Bu_3SnH plus 5 mol % AIBN to **2** (0.2 mmol/min).

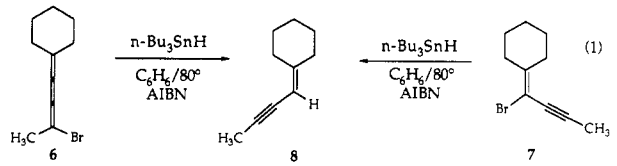
0022-3263/90/1955-2983$02.50/0

Table I. Cyclization of Bromo[3]cumulenes in Benzene at 80 °C

entry	cumulene	products(s)/isolated yield
A		 43%
B		 45%
C		 41% Diastereomeric ratio 1:1
D		 16%

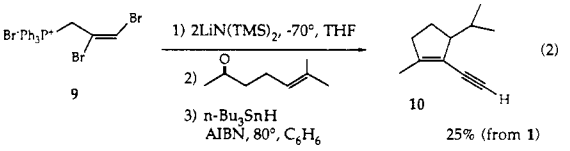
reaction conditions. Quenching with *n*-Bu_3SnH gives **4** as the only detectable product.[9]

It is interesting to note that a simple bromo[3]cumulene with no olefinic tether is reduced to the enyne by *n*-Bu_3SnH. Thus, cyclohexanone-derived bromo[3]cumulene **6** or its isomeric bromo enyne **7**[2] gave exclusively **8** under those conditions shown in eq 1.



Selected examples that demonstrate similar cyclization behavior are presented in Table I. The isolated product yield in each case reflects a two-step conversion based on phosphonium salt **1**. The 5-(*π-Endo*)-*Exo-Trig* product is seen in entry A. The bromo[3]cumulene ester of entry B was a mixture of all possible geometric isomers. This, of course, mattered little as only a single cyclization product reflecting the 5-(*π-Endo*)-*Exo-Trig* mode realistically could form here. A small amount of what appeared to be the acyclic reduced product, as determined by GC/MS, also was seen. As expected a 1:1 diastereomeric mixture of products was isolated from the cumulene (derived from **1** and geranylacetone) in entry C. An extension of this method is the preparation of a bromo[3]cumulene with a tethered acetylenic group. The terminal acetylene in entry D cyclized in poor yield. The product was very unstable, which impeded complete characterization.[11]

The method, as demonstrated, offers flexibility in product design by virtue of the choice in ketone substrate. Added synthetic utility can be achieved through the choice of other dibromoallylic phosphonium salts such as **9**. The terminal acetylene **10** is produced in the usual two-step sequence in somewhat lower yield than **4** (from **1**)[12] (eq 2).



Thus, a novel two-step cyclopentenyne synthesis has been developed based on the intermediacy of bromo[3]-cumulenes. The method, though not proven here, should be amenable to the preparation of fused ring systems.

Experimental Section

Melting points were determined in open capillary tubes on a Mel-Temp apparatus and are uncorrected. The following were used for spectral characterizations: ultraviolet spectra, Hewlett Packard 8450 diode array spectrophotometer; mass spectra, (EI) VG ZAB-SE spectrometer; IR spectra FT Nicolet 7199 spectrometer. ^1H (300 and 500 MHz) and ^{13}C (75 or 125 MHz) NMR spectra were recorded on a GE GN-500 spectrometer or Nicolet NT-300 WB spectrometer. Analtech silica gel GF plates (250 mm) were used for thinlayer chromatography. Silica gel (300–400 mesh), Merck kieselgel 60, or Florisil (200–300 mesh) (Fluka) were employed for flash column chromatography. Solvents used were from freshly opened bottles of spectroscopy grade quality with no special drying procedures observed.

Each cyclized product was purified via silica gel flash column chromatography and then scrutinized for purity on a Hewlett-Packard 5890 gas chromatograph interfaced to a Finnigan MAT 710 ion-trap detector (ITD). The GC was configured with two parallel fused silica capillary columns, 30 m × 0.25 mm i.d., coated with 0.25-μm DB-5. The column oven was maintained at 35 °C for 2 min, then increased at 10 °C/min to 220 °C. Concentrations (w/w %) were estimated by using FID area % renormalized to exclude the solvent peaks.

(*trans*-2,3-Dibromo-2-butenyl)triphenylphosphonium Bromide (1). The synthesis of **1** was analogous to that described for (*trans*-2,3-dibromo-3-phenyl-2-propen-1-yl)triphenylphosphonium bromide reported in ref 1. From 2-butyn-1-ol, salt **1** was prepared in 73% overall yield: mp 190–193 °C (cold CH_2Cl_2/C_6H_{14}); ^1H NMR ($CDCl_3$) δ toluene impurity 2.27 (d, 3 H, CH_3, J = 5 Hz), 5.55 (d, 2 H, CH_2, J = 14 Hz), 7.6–7.8 (m, 15 H); ^{31}P NMR ($CDCl_3$) δ + 26.3; IR (KBr) H_2O impurity ν_{max} cm^{-1} 3050, 3010, 2820, 2750, 1625, 1585, 1440; MS (HR FAB/PEG 459) for $C_{22}H_{20}Br_2P$ calcd 472.9671, found 472.9669. Anal. Calcd for $C_{22}H_{20}Br_3P$: C, 47.60; H, 3.63; Br, 43.19; P, 5.58. Found: C, 47.55; H, 3.69; Br, 42.94; P, 5.83.

(*trans*-2,3-Dibromo-2-propenyl)triphenylphosphonium Bromide (9). Salt **9** was prepared in 68% overall yield from propargyl alcohol: mp 158–162 °C (cold CH_2Cl_2/C_6H_{14}); ^1H NMR ($CDCl_3$) δ 5.6 (d, 2 H, CH_2, J = 15 Hz), 6.7 (d, 1 H, vinyl, J = 4.5 Hz), 7.5–8.1 (m, 15 H); ^{31}P NMR ($CDCl_3$) δ +24.8; IR (KBr) H_2O impurity ν_{max} 3050, 3010, 2840, 2820, 2760, 1620, 1580, 1480; MS (HR FAB) for $C_{21}H_{18}Br_3P$ (calcd 458.9510, found 458.9513. Anal. Calcd for $C_{21}H_{18}Br_2P$: C, 46.62; H, 3.35; Br, 44.30; P, 5.72. Found: C, 47.39; H, 3.32; Br, 40.70; P, 5.53.

(*E* and *Z*)-4-Bromo-5,9-dimethyl-4,8-decadien-2-yne (3). Enyne **3** was prepared from 6-methyl-5-hepten-2-one and salt **1** via the intermediacy of cumulene **2**. Compound **2** was isomerized

(9) One, however, cannot completely discount the possibility that the cumulene **2** undergoes first a thermal isomerization in the presence of *n*-Bu_3SnH/*n*-Bu_3SnBr to the bromo enyne **3**, which is then converted to a vinyl radical. In one experiment, **2** was refluxed with *n*-Bu_3SnBr under argon in benzene for 1.5 h, giving approximately 10% conversion to **3**, the remainder being unconverted **2** (≈70%) and uncharacterized components (≈20%) based on ^1H NMR and IR data.

(10) See: Beckwith, A. L. J., in ref 6 and Stork, G.; Mook, R., Jr. *Tetrahedron Lett.* **1988**, *27*, 4529.

(11) This product was unstable when concentrated, even when kept cold. Attempts to exhaustively hydrogenate with Raney nickel only produced complicated mixtures that eluded characterization. Nevertheless, ^1H NMR, IR, and MS data are given in the Experimental Section.

(12) Cyclopentenyne **10** was extremely volatile and difficulty was experienced in separating it from solvent. Compounding this problem was its instability when concentrated at room temperature. On the other hand, **4** was less volatile but showed similar instability.

with CuBr to **3** in 58% overall yield from **1**. The generalized procedure for this two-step process has been reported.[2] **3**: ^{1}H NMR (C_6D_6) E/Z mixture δ 1.51, 1.53 (2 s, 3 H, propargyl methyl, ratio 1:1), 1.55–1.84 (6 s, 9 H, 3 allylic methyls of equal ratio), 2.1 (dd, 2 H, allylic, J = 15 and 8 Hz), 2.25 (t, 1 H, allylic, J = 8 Hz), 2.35 (t, 1 H, allylic, J = 8 Hz), 5.13 (m, 1 H, vinyl); ^{13}C (C_6D_6) δ 4.0 (propargyl methyl), 17.5, 17.6, 21.2, 22.0, 25.8 (2) (allylic methyls), 25.75, 26.66, 37.2, 37.7 (allylic methylenes), 78.3, 78.6, 90.5, 90.6 (acetylenic carbons), 98.4, 99.2 (vinyl carbon), 123.6, 128.3 (vinyl methine), 132.2, 132.3, 145.1, 145.5 (2 vinyl carbons); IR (neat) ν_{max} cm^{-1} 3040, 2960, 2840, 2210 (acetylene), 1430; MS (HREI) for $C_{12}H_{17}Br$ calcd 240.0516, found 240.0516; UV (hexane) λ (ϵ) 236 (9800).

1-Methyl-3-(1-methylethyl)-2-(1-propynyl)cyclopentene (4) via the Bromo[3]cumulene 2. The bromo[3]cumulene **2** was prepared from the phosphonium salt **1** (3.5 g, 6 mmol) and 6-methyl-5-hepten-2-one (1.0 g, 8 mmol) in 25 mL of THF as in ref 2. Purification of **2** using flash column chromatography (Florisil–hexane) gave a colorless oil, which was extremely unstable when concentrated at room temperature: ^{1}H NMR (C_6D_6) E/Z mixture (1:1) δ methyl singlets at 1.50, 1.53, 1.54, 1.55, 1.62, 1.74 (9 H, 3 CH_3), 1.93 (dd, 2 H, allylic methylene, J = 14 Hz and 8 Hz), 2.13 (dd, 2 H, allylic methylene, J = 16 Hz and 8 Hz), 2 methyl singlets at 2.20, 2.22 (3 H), 5.13 (m, 1 H, vinyl H); ^{13}C NMR (C_6D_6) E/Z mixture 17.7, 17.78, 21.95, 22.53, 25.75, 25.79, 26.35, 26.38, 28.24, 28.51, 37.56, 37.60, 91.49, 91.56, 117.69, 123.88, 123.98, 128.29, 132.04, 132.10, 4 cumulene carbon signals at 155.26, 155.48, 156.45, 156.48; IR (neat) ν_{max} cm^{-1} 2966, 2913, 2857, 2057 (cumulene), 1658, 1436, 1369, 1066; UV (hexane) λ (ϵ) 273 (14 200), 257 (16 000), 205 (21 600); MS (LREI) no molecular ion seen.

The cumulene **2**, in 175 mL of benzene along with AIBN (31 mg) and n-Bu_3SnH (1.1 g, 3.8 mmol) was refluxed under an argon atmosphere for 20 min. The reaction was cooled and then the solvent was removed in vacuo. Chromatography on flash silica (hexane) gave 408 mg of **4** (42% overall from **1**): ^{1}H NMR ($CDCl_3$) δ 0.76 (d, 3 H, CH_3, J = 6.8 Hz), 0.93 (d, 3 H, CH_3, J = 6.9 Hz), 1.55 (m, H_5), 1.8 (m, H_4), 1.83 (d, 3 H, allylic methyl, J = 1.4 Hz), 2.05 (m, H_3), 2.02 (s, 3 H, propargyl methyl), 2.25 (t, 2 H, 2 H_5), 2.65 (m, 1 H, allylic methine); ^{13}C NMR ($CDCl_3$) δ 4.4 (propargyl methyl), 15.74, 16.56, 20.8, 23.1, 29.77, 36.96, 54.33, 76.38, and 89.15 (2 acetylenic carbons), 121.83 and 145.87 (2 vinylic carbons); IR (neat) ν_{max} cm^{-1} 2230 (acetylene); UV (hexane) λ (ϵ) 235 (24 000); MS (EI), m/e (relative intensity) 162 (M^+, 40), 119 (M^+ – isopropyl, 95), 91 (100); MS-HREI for $C_{12}H_{18}$ calcd 162.1409, found 162.1406; GLC (t_R) 13.02 min (98.8% pure).

Cyclopentene 4 via the Bromo Enyne 3. The bromo enyne **3** (840 mg, 3.5 mmol), n-Bu_3SnH (1.1 g, 3.8 mmol), and AIBN (31 mg) were dissolved in 175 mL of benzene (0.02 M) and refluxed under argon for 20 min. The reaction was cooled and then the solvent was removed in vacuo. Flash column chromatography on silica gel (hexane) gave 480 mg (85%) of **4** as a colorless oil, which was 97.2% pure by GLC analysis.

1,3-Dimethyl-2-(1-propynyl)cyclopentene (Table I, Entry A). This cyclopentene was prepared in 43% overall yield from salt **1** and 5-hexen-2-one via the bromo[3]cumulene as described for **4**: ^{1}H NMR ($CDCl_3$) δ 1.07 (d, 3 H, CH_3, J = 7 Hz), 1.37 (m, H_4), 1.82 (d, 3 H, propargyl methyl, J = 1.5 Hz), 2.05 (s, 3 H, allylic methyl), 2.07 (m, 1 H, CH), 2.28 (m, allylic methylene), 2.69 (m, 1 H, allylic methine); ^{13}C NMR ($CDCl_3$) δ 4.5 (propargyl methyl), 16.0, 20.1, 31.6, 36.5, 43.0, 75.95, 89.4, 124.0, 145.0; MS (EI), m/e (relative intensity) 134 (M^+, 50), 119 (M^+ – CH_3, 100), 91 (87), 77 (30); GLC t_R = 10.2 (89% pure); IR (neat) ν_{max} cm^{-1} 2210 (weak); UV (hexane) λ (ϵ) 234 (21 000); MS-HREI calcd 134.1095, found 134.1082.

1-Methyl-3-(1,5-dimethylhex-4-enyl)-2-(1-propynyl)cyclopentene as a Diastereomeric Mixture (Table I, Entry C). As described in ref 2, lithium bis(trimethylsilyl)amide (6 mmol as a 1 M THF solution) was added dropwise to a THF suspension (12 mL) of phosphonium salt **1** (1.75 g, 3 mmol) at –70 °C under argon. The ylide solution was stirred for 20 min, while the temperature rose to –60 °C. Geranylacetone (0.68 g, 3.5 mmol) was added dropwise and the resulting solution was stirred for 1 h while the temperature rose to –10 °C. Dilution of the reaction mixture with Et_2O (50 mL) followed by filtration through a plug of Florisil gave the crude intermediate bromo[3]cumulene. The solution of the crude bromo[3]cumulene was dried (Na_2SO_4), then reduced in volume (90%), followed by the addition of benzene (20 mL). After degassing this solution with argon, a benzene solution of n-Bu_3SnH and AIBN (5 mol %) was added via syringe pump (1.64 mmol/h for 2.5 h) to this solution, at reflux, under argon.

On workup the reaction solvent was removed followed by purification via flash chromatography (silica gel–hexane) to give 0.284 g (41%) of product cyclopentene: bp 90 °C/0.2 mm; ^{1}H NMR ($CDCl_3$) 1:1 diastereomeric mixture δ 2 sets of methyl doublets at 0.725 and 0.9 (3 H, J = 7 Hz), 1.03 (m, 1 H), 1.3 (m, 2 H), 1.55 (m, 1 H), 1.62 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.81 (s, 3 H, CH_3), 1.83 (m, 2 H, 1.95 (m, 1 H), 2.03 (s, 3 H, CH_3), 2.25 (br t, 2 H, allylic methylene), 2.75 (m, 1 H, allylic methine), 5.15 (t, 1 H, vinyl H); UV (hexane) λ (ϵ) 235 (29 600); MS (EI), m/e (relative intensity) both diastereomers had virtually identical fragmentation patterns, 230 (M^+, 50), 215 (M^+ – CH_3, 50), 159 (70), 119 (100), 91 (50); GLC (t_R) 18.95 min and 19.16 min (ratio 51.4:43.5, total purity 95%). Anal. Calcd for $C_{17}H_{26}$: C, 88.62; H, 11.67. Found: C, 88.47; H, 11.10.

2-Butynylidenecyclohexane (8) from 1-Bromo-2-butynylidenecyclohexane (7). To the bromo enyne **7**[2] (430 mg, 2.1 mmol), dissolved in benzene (95 mL), were added n-Bu_3SnH (0.61 g, 2.1 mmol) and AIBN (30 mg). The solution was heated at reflux under argon for 20 min. The solution was then cooled and the solvent removed. The product **8**, an oil, was obtained pure (190 mg, 75% or 49% from salt **1**), following flash column chromtography (hexane): bp 50 °C/0.2 mm (Kugelrohr distillation); ^{1}H NMR ($CDCl_3$) δ 1.5 (m, 6 H, 3 CH_2), 1.96 (s, 3 H, CH_3), 2.13 (m, 2 H, allylic methylene), 2.36 (m, 2 H, allylic methylene), 5.15 (m, 1 H, vinyl H); ^{13}C NMR ($CDCl_3$) δ 4.2 (propargyl methyl), 26.3, 27.4, 28.2, 31.2, 35.7 (5 CH_2), 87.0 (acetylenic carbon), 101.7 (CH), 153.83; IR (neat) ν_{max} cm^{-1} 3010, 2910, 2830, 2200, 1620, 1440; MS (EI), m/e (relative intensity) 134 (M^+, 30), 119 (M^+ – CH_3, 13), 105 (20), 91 (80), 68 (100); GLC (t_R) 12.37 min (99.1%); UV (hexane) δ (ϵ) 234 (21 800). Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.70; H, 10.55.

Enyne 8 from the Bromo[3]cumulene 6. The bromo[3]cumulene **6** was prepared from the salt **1** (1.75 g, 3 mmol) and cyclohexanone (0.390 g, 4 mmol) as described in ref 2: ^{1}H NMR ($CDCl_3$) δ 1.6 (br s, 6 H, 3 CH_2), 2.2 (br t, 4 H, 2 allylic CH_2), 2.3 (s, 3 H, CH_3); IR (neat) ν_{max} cm^{-1} 2050 (cumulene). This intermediate **6** was subjected to the same n-Bu_3SnH reducing conditions as **7** to give **8**, 0.18 g (45% from **1**).

1-Methyl-3-methylene-2-(1-propynyl)cyclopentene (Table I, Entry D). The bromo[3]cumulene was isolated in crude form from salt **1** (3.5 g, 6 mmol) and 5-hexyn-2-one[13] (0.34 g, 3.5 mmol) as described previously:[2] IR (neat) ν_{max} cm^{-1} 3280 (C≡CH), 2960, 2900, 2830, 2100 (C≡C), 2050 (cumulene), 1650. Treatment of the crude cumulene with the same cyclization conditions used to prepare **4** gave after a 4-h reaction time 0.05 g of cyclopentene product (16% based on salt **1**) as an unstable oil: ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3 H, propargyl methyl), 2.08 (s, 3 H, allylic methyl), 2.42 (m, 2 H, allylic methylene), 2.58 (m, 2 H, allylic methylene), 4.75 (br s, 1 H, vinylic H), 5.0 (br s, 1 H, vinylic H); ^{13}C NMR ($CDCl_3$) δ 4.4 (propargylmethyl), 16.6, 28.9, 35.64 (allylic carbons), 72.9 and 91.35 (acetylenic carbons), 100.4 (terminal methylene carbon), 123.4, 154.0, 154.2 (vinylic carbons); small impurity absorbancies at 30.3, 43.9, 111.0, 123.1, and 125.5; MS (EI), m/e (relative intensity) 132 (M^+, 75), 117 (M^+ – CH_3, 60), 115 (100), 91 (80); HREI for $C_{10}H_{12}$ calcd 132.0941, found 132.0939.

1-Methyl-3-(2-propyl)-2-ethynylcyclopentene (10). Cyclopentene **10** was prepared in 25% yield from phosphonium salt **9** and 6-methyl-5-hepten-2-one as was described for **4**: ^{1}H NMR ($CDCl_3$) δ 0.76 (d, 3 H, CH_3, J = 7 Hz)8 0.93 (d, 3 H, CH_3, J = 7 Hz), 1.45–1.65 (m, 1 H), 1.75–1.90 (m, 1 H), 1.83 (d, 3 H, allylic methyl, $J_{H\text{-}CH_3}$ = 1.4 Hz), 1.95–2.1 (m, 1 H), 2.3 (t, 2 H, allylic methylene), 2.7 (m, 1 H, allylic methine), 3.1 (s, 1 H, acetylenic H); impurities at 0.7, 1.25, 4.8, 5.1; IR (neat) ν_{max} cm^{-1} 3290 (s), 2900 (s), 2070 (s), 1620, 1450, 1430; MS (EI), m/e (relative intensity) 148 (M^+, 15), 133 (M^+ – CH_3, 12), 105 (M^+ – isopropyl, 100), 91 (20), 79 (60); GLC (t_R) 10.42 min (86.2%); HREI for $C_{11}H_{16}$ calcd 148.1253, found 148.1252.

1,3-Dimethyl-2-(1-propynyl)-2-cyclopentene-1-acetic Acid, Ethyl Ester (Table I, Entry B). This compound was prepared

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from phosphonium salt 1 and ethyl 3-methyl-6-oxo-2-heptenoate (E/Z = 3) in identical fashion as described for 4. The ethyl 3-methyl-6-oxo-2-heptenoate was prepared by a Wittig synthesis involving 2,5-hexanedione (2 equiv) and the ylide formed from 1 equiv of triethyl phosphonoacetate (NaH, 1 equiv) in THF at 0 °C followed by purification by flash silica column chromatography: ^{1}H NMR ($CDCl_3$) E/Z isomers δ 1.3 (t, 3 H, CH_3), 2.16, 2.17 (two singlets, 6 H, 2 CH_3), 2.4 and 2.82 (2 triplets, 2 H, allylic CH_2), 2.65 (t, 2 H, CH_2 α to 6-oxo), 4.15 (q, CH_2O), 5.65 and 5.70 (2 singlets, 1 H, vinylic hydrogens, ratio 3:1 respectively); IR (neat) ν_{max} cm^{-1} 2982, 2939, 2907, 1716, 1650; MS (DCI-ammonia) m/e (relative intensity) 202 (M^+ + 18, 100), 185 (M^+ + 1, 75).

The product cyclopentene in this reaction was partially purified via flash silica gel column chromatography (10% EtOAc-90% hexane eluent) to give 380 mg of product, which proved to be 77% pure by GLC analysis (adjusted yield 45%): ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 3 H, CH_3), 1.25 (t, 3 H, CH_3), 1.7 (m, 1 H, cyclopentene H_4), 1.8 (s, 3 H, propargyl CH_3), 2.0 (s, 3 H, allylic methyl), 2.1 (m, 1 H, cyclopentene H_4), 2.3 (m, 2 H, cyclopentene H_5), 2.4 (dd, 2 H, CH_2CO_2Et, J = 56 and 13 Hz), 4.1 (m, 2 H, CH_2O); ^{13}C NMR ($CDCl_3$) δ 4.5 propargyl methyl, 14.3, 16.0, 25.1, 35.5, 35.6, 44.2, 49.4, 59.9, 74.4, 90.3, 126.7, 144.59, 172.8; IR (neat) ν_{max} cm^{-1} 2962, 2912, 2210 (w), 1734 (CO); MS (EI), m/e (relative intensity) 220 (M^+, 22), 147 ($M^+ - CO_2Et$, 90), 133 (100), 117 (90), 105 (60), 91 (80); GLC (t_R) 17.9 min; MS-HREI, calcd 220.1463, found 220.1464.

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Supplementary Material Available: ^{13}C and ^{1}H NMR spectra for compounds **2-4**, and **10** and entries A, B, and D of Table I. (10 pages). Ordering information is given on any current masthead page.

Photochemical Reactions of Semicyclic Monothioimides. A Novel Photocyclization of *N*-(β,γ-Unsaturated Carbonyl) Thioamides

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The photochemistry of the nitrogen-containing thiocarbonyl compounds have received much attention from both synthetic and mechanistic viewpoints. In particular, the Paterno-Büchi reactions of thioamides[1] and thioimides[2] have been investigated for this purpose. In relation to our study on the photochemical reactions of acyclic and semicyclic monothioimides,[3] we now report on the photoreactions of *N*-(β,γ-unsaturated carbonyl) thioamides. We previously reported on the photochemistry of *N*-(α,β-unsaturated carbonyl) thioamides, which proceeded via an intramolecular [2 + 2] photocyclization to produce thietane-fused β-lactams in good yields.[3a] In contrast, we now report that the introduction of one carbon atom between the olefin and carbonyl group produced many differences in the photochemical properties.

Scheme I

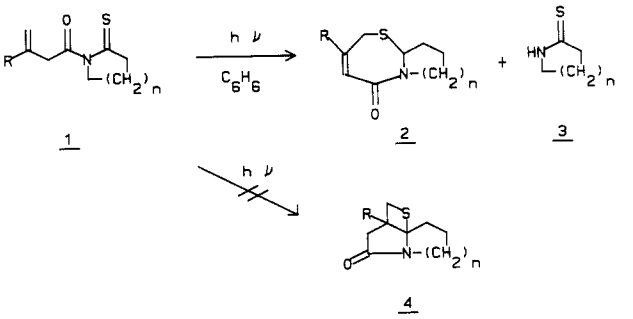

Table I. Photolysis of Monothioimides 1a-f

	n	R	yield, % 2	yield, % 3
a	1	H	24	31
b	1	Me	61	34
c	2	H	71	trace
d	2	Me	56	trace
e	3	H	38	trace
f	3	Me	46	trace

Results and Discussion

The monothioimides **1a-f** were obtained by condensation of the corresponding acids with thiolactams in the presence of DCC, whereas the monothioimides **1g,h** were synthesized from acid chlorides and thiolactams, using triethylamine as base. When *N*-(3-butenoyl)thiopyrrolidone (**1a**) was irradiated in benzene with a 1-kW high-pressure mercury lamp under nitrogen until the starting material had disappeared, 2-oxo-6-thia-1-azabicyclo[5.3.0]dec-3-ene (**2a**) was obtained in 24% yield, accompanied by thiopyrrolidone **3** (n = 1) (Scheme I). The structure of **2a** was determined on the basis of elemental analysis and spectral data. The IR spectrum ($CHCl_3$) exhibited an absorption at 1660 cm^{-1} (C=O). The ^{1}H NMR spectrum ($CDCl_3$) of the product showed new signals arising from olefinic protons at δ 6.0-6.4 (m, 2 H). The ^{13}C NMR spectrum ($CDCl_3$) exhibited three doublet signals at δ 60.5 (d), 128.9 (d), and 131.6 (d), assigned to C-7, C-3, and C-4, respectively. Furthermore, the ^{13}C NMR spectrum evidenced the disappearance of the thiocarbonyl group. The structure of thiopyrrolidone **3** was determined by comparison with an authentic sample. Photolysis of thioimides **1b-f** under the same conditions also gave the corresponding bicyclic lactams **2b-f** as shown in Table I. In these reactions, thietane **4** was not detected at all.

The formation of the bicyclic lactams **2** is reasonably explained in terms of the generation of 1,4-diradical intermediate **5** as shown in Scheme II. Presumably, the strain energy required to form thietane **4** prevents closure of diradical intermediate **5** and leads to bicyclic lactams **2** via a 1,4-hydrogen shift. We were unsuccessful in

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